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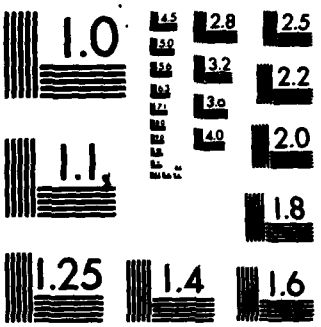

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
This report summarizes research to establish the high-resolution spectroscopy and detailed mechanisms of sequences of resonant transitions induced in atoms and molecules by multicolor, multiphoton excitation. These processes are studied as a function of the independently tunable frequencies and polarization states of multiple dye laser beams in order to establish both the underlying physics and the high degree of selectivity of this advanced form of laser excitation. Detection methods include photoelectron analysis, mass →

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spectrometry, and laser-induced fluorescence. During this period, all instrumentation needed for this research was put into full operation and was used to examine multiphoton ionization processes in H_2, CO, and N_2. For example, a novel, totally-state-selected process was studied in H_2 in which a single rotational, vibrational level of the target gas was excited by three-photon excitation to a single rotational, vibrational level of the $B\,^1\Sigma_u^+$ state of H_2, followed by single-photon ionization. The ejected electrons were then energy analyzed with rotational resolution, yielding the first rotationally resolved study of photoionization of an excited molecular state. Multicolor studies are now beginning, and an improved electron spectrometer system is being developed to greatly enhance the resolution/sensitivity of these studies.

ANNUAL SUMMARY REPORT

High-Resolution Spectroscopy and Dynamics of Multiphoton Processes in Atoms and Molecules (Contract Nos. N00014-82-F-0074 and N00014-83-F-0001)

Submitted to

Office of Naval Research
Physical Sciences Division
Physics Program Office
Department of the Navy
Arlington, VA 22217

ATTN: Dr. Bobby R. Junker

Submitted by

Argonne National Laboratory
Argonne, IL 60439
15 June 1983

1. Principal Investigators

Dr. Patricia M. Dehmer
Argonne National Laboratory
Argonne, IL 60439
Tel: 312-972-4187

Dr. Joseph L. Dehmer
Argonne National Laboratory
Argonne, IL 60439
Tel: 312-972-4194

2. Contract Description

This contract covers research to establish the high-resolution spectroscopy and detailed mechanisms of sequences of resonant transitions induced in atoms and molecules by multicolor, multiphoton excitation. These processes are studied as a function of the independently tunable frequencies and polarization states of multiple dye laser beams in order to establish both the underlying physics and the high degree of selectivity of this advanced form of laser excitation.

3. Scientific Problem

This study is aimed at both determining the underlying physics and developing the high degree of selectivity of multicolor, multiphoton processes in atoms and molecules. This is a frontier research area which involves roughly three major challenges: First, it is necessary to establish the spectroscopy of excited states of molecules at vastly improved resolution. This results from the narrow line width of tunable dye lasers, typically 0.02-0.10 cm^{-1} for pulsed sources. This means that, in molecules, intermediate states of resonant excitation sequences will correspond to particular excited rotational-vibrational-electronic states of the molecule. Therefore, to specify a workable sequence of resonant transitions, it is necessary to know the excited state spectroscopy at this level. Second, it is necessary to establish the mechanisms and dynamical parameters governing multiphoton processes. For example, in order to design the most selective and sensitive excitation scheme, one must learn the cross sections for successive steps, rates and modes of decay of intermediate states, and cross sections for all competing excitation sequences, including non-resonant ones. This requisite basis for selective excitation is largely unknown at this time and requires a concerted basic research effort for adequate development. Third, this work involves harnessing the rapid technological advances in lasers, optics, and electronics to produce a composite laser probe which can stimulate a preselected sequence of resonant steps within the five nanosecond duration of the laser pulse.

4. Scientific and Technical Approach

This program utilizes a complementary set of experimental techniques to address the problems described above. The total experimental facility can be summarized in terms of its six major components: (1) A Nd:YAG oscillator/amplifier is used as the pump laser for all the dye lasers used to produce the composite laser beam. (2) We currently have three dye laser

oscillator/amplifiers to produce three laser beams with independently tunable frequencies and polarization states. One laser is a commercial laser outfitted with nonlinear conversion (frequency doubling and summing) capability for producing ultraviolet frequencies. Two other dye lasers were manufactured to produce narrow line width visible beams for probing transitions among upper states. (3) A time-of-flight mass spectrometer is used to measure the ionic products of multiphoton ionization. (4) A high-resolution hemispherical electron spectrometer is used to analyze the kinetic energies of the electrons produced by multiphoton ionization. (5) A fluorescence spectrometer is used to monitor fluorescence from laser excited states throughout the excitation chain. (6) The multiple control and detection channels are centrally controlled by a microprocessor.

Summarizing, we are able to probe atoms and molecules with a fully flexible composite laser probe and measure most major excitation products - ions, electrons, and fluorescence. The remaining major product, namely neutral fragments, could also be monitored by further ionization or by laser-induced fluorescence, but this is not in our initial plans. Spectroscopic and dynamical information is then obtained by monitoring these detection channels as a function of the frequencies and polarization states of the input composite laser probe.

5. Progress

Following the completion of all major facilities for this project during the last (initial) contract period, this contract period was very productive. Much of the progress is reflected in the papers, abstracts, and talks listed in Section 6 (to which we will refer by paper number in this section). Briefly, the progress can be summarized in three categories. First, several multiphoton ionization studies, with mass and electron energy analysis, were performed on small molecules of fundamental interest, namely, H_2 (paper 8), CO (papers 6 and 12) and N_2 (in preparation). Our concentration on small, difficult-to-ionize molecules of basic importance with advanced secondary detection such as electron energy analysis, is still unique in the field of multiphoton ionization. These studies have explored the dynamics of multiphoton ionization in a very powerful way and, in so doing, have paved the way for our multicolor (multiple laser beam) studies, which are just getting underway. Of particular importance is the first-of-its-kind state-selected study (paper 8), in which H_2 was excited to a single rotational, vibrational level of the $B\ ^1\Sigma_u^+$ excited state, followed by single-photon ionization and rotationally resolved photoelectron energy analysis. This example is the prototype of the experiments we plan to do on a whole range of molecules with our multicolor laser probe. Second, several advancements were made in our instrumentation, including a second frequency doubling device (so we can use two frequency-doubled beams) and a Fizeau wavemeter for absolute wavelength calibration. Also, a conceptual design for an optically-coupled area detector has been completed. This will be utilized with a recently completed 4-inch, mean-radius hemispherical analyzer to vastly improve the resolution/sensitivity of our electron detection channel. Third, several secondary studies on single-photon molecular photoionization (papers 1-5, 7, 9-11) have been carried out and prepared for publication.

6. Publications

The papers, abstracts of conference presentations, and invited talks prepared with the support of this contract are listed on the following pages.

PAPERS

1. P. M. Dehmer, and J. L. Dehmer, "Observation of Bending Modes in the $X\ ^2\Pi_u$ State of the Acetylene Ion Using HeI Photoelectron Spectrometry," J. Electron Spectrosc. 28, 145 (1982).

2. E. D. Poliakoff, P. M. Dehmer, J. L. Dehmer, and R. Stockbauer, "Photoelectron-Photoion Coincidence Spectroscopy of Gas-Phase Clusters," J. Chem. Phys. 76, 5214 (1982).

3. P. M. Dehmer and S. T. Pratt, "Photoionization of ArKr, ArXe, and KrXe and Bond Dissociation Energies of the Rare Gas Dimer Ions," J. Chem. Phys. 77, 4804 (1982).

4. P. M. Dehmer, "Dissociation in Small Molecules," Desorption Induced by Electronic Transitions, Eds. N. H. Tolk, M. M. Traum, J. C. Tully, and T. E. Madey (Springer-Verlag, Berlin, 1982), p. 164.

5. P. M. Dehmer and S. T. Pratt, "VUV Spectroscopy of Rare Gas van der Waals Dimers," in Photophysics and Photochemistry in the Vacuum Ultraviolet, edited by S. McGlynn, G. Findley, and R. Huebner (D. Reidel Publ., Dordrecht, Holland, 1983), in press.

6. S. T. Pratt, E. D. Poliakoff, P. M. Dehmer, and J. L. Dehmer, "Photoelectron Studies of Resonant Multiphoton Ionization of CO via the $A\ ^1\Pi$ State," J. Chem. Phys. 78, 65 (1983).

7. E. D. Poliakoff, J. L. Dehmer, P. M. Dehmer, and A. C. Parr, "Vibrationally-Resolved Photoelectron Angular Distributions for H_2," Chem. Phys. Lett. 96, 52 (1983).

8. S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, "Resonant Multiphoton Ionization of H_2 via the $B\ ^1\Sigma_u^+$, v=7, J=2 and 4 Levels with Photoelectron Energy Analysis," J. Chem. Phys. 78, 4315 (1983).

9. S. T. Pratt and P. M. Dehmer, "On the Dissociation Energy of $ArCO_2^+$," J. Chem. Phys., in press.

10. P. M. Dehmer, "Rydberg States of van der Waals Molecules — A Comparison with Rydberg States of Atoms and of Chemically-Bonded Species," Comments At. Mol. Phys., in press.

11. P. M. Dehmer and W. A. Chupka, "Photoabsorption and Photoionization of HD," J. Chem. Phys., in press.

12. S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, "Two Photon Resonant, Four Photon Ionization of CO via the $A^1\Pi$ State with Photoelectron Energy Analysis," J. Chem. Phys., submitted for publication.

ABSTRACTS OF CONFERENCE PRESENTATIONS

1. J. L. Dehmer, E. D. Poliakoff, and P. M. Dehmer, "Photoelectron Angular Distributions From Multiphoton Ionization. Seven Photon Ionization of Kr at 532 nm," XIII DEAP Meeting, 3-5 December 1981, New York, N.Y., Bull. Am. Phys. Soc. 26, 1322 (1981).

2. E. D. Poliakoff, P. M. Dehmer, J. L. Dehmer, and R. Stockbauer, "Photoelectron-Photoion Coincidence Spectroscopy of Gas-Phase Clusters," XIII DEAP Meeting, 3-5 December 1981, New York, N.Y., Bull. Am. Phys. Soc. 26, 1322 (1981).

3. P. M. Dehmer and S. T. Pratt, "Systematics of Electronic Structure in Rare Gas van der Waals Molecules," Abstract of an Invited Talk at the NATO Advanced Study Institute on Photophysics and Photochemistry in the Vacuum Ultraviolet, 15-28 August 1982, Lake Geneva, WI, Book of Abstracts.

4. S. T. Pratt, E. D. Poliakoff, P. M. Dehmer, and J. L. Dehmer, "Photoelectron Studies of Resonant and Nonresonant Multiphoton Ionization Processes," Contributed talk at the Gordon Conference on UV/Visible Multiphoton Ionization and Dissociation Processes, 12-16 July 1982 (no abstract available).

5. P. M. Dehmer, "VUV Spectroscopy of Rare Gas van der Waals Dimers," (invited talk), Proceedings of the 2nd European Workshop on Molecular Spectroscopy and Photon-Induced Dynamics, September 27-30, 1982, Flevopolder, The Netherlands, AMOLF-Report #83-3, p. 11.

6. J. L. Dehmer, P. M. Dehmer, and S. T. Pratt, "Multiphoton Ionization as a Probe of Molecular Photoionization Dynamics," (invited talk), Proceedings of the U.S./Japan Seminar on Electron-Molecule Collisions and Photoionization Processes, 26-29 October 1982, Pasadena, California, p. 18.

7. S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, "Resonant Multiphoton Ionization of H_2 via the B $^1\Sigma_u^+$ State with Photoelectron Energy Analysis," XIV DEAP Meeting, 23-25 May 1983, Boulder, CO, Bull. Am. Phys. Soc. 28, 808 (1983).

8. P. M. Dehmer, S. T. Pratt, E. D. Poliakoff, and J. L. Dehmer, "Photoelectron Studies of Resonant Multiphoton Ionization of CO via the A $^1\Pi$ State," ibid., p. 792.

9. P. M. Dehmer, "Decay of Rydberg States via Autoionization and Predissociation," ibid., p. 779.

10. S. T. Pratt, E. D. Poliakoff, P. M. Dehmer, and J. L. Dehmer, "Photoelectron Studies of Resonant Multiphoton Ionization of CO via the A $^1\Pi$ State," Proceedings of the XIII International Conference on the Physics of Electronic and Atomic Collisions, July 27 - August 2, 1983, Berlin, Germany, p. xx.

ABSTRACTS OF CONFERENCE PRESENTATIONS - Continued

11. S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, "Resonant Multiphoton Ionization of H_2 via the B $^1\Sigma_u^+$, v = 7, J = 2 and 4 Levels with Photoelectron Energy Analysis," ibid., p. xx.

INVITED TALKS, COLLOQUIA, AND SEMINARS

1. P. M. Dehmer, "Systematics of Electronic Structure within Families of van der Waals Molecules as Revealed by VUV Spectroscopy," Interdisciplinary Physical Sciences Seminar, Yale University, 30 November 1981.

2. P. M. Dehmer, "Systematics of Electronic Structure in Rare Gas van der Waals Molecules," Chemistry Department Seminar, Brookhaven National Laboratory, 19 January 1982.

3. P. M. Dehmer, "Systematics of Electronic Structure Within Families of van der Waals Molecules as Revealed by VUV Spectroscopy," Atomic and Molecular Sciences Seminar, Argonne National Laboratory, 18 February 1982.

4. P. M. Dehmer, "Systematics of Electronic Structure Within Families of van der Waals Molecules," Chemistry Department Colloquium, Illinois Institute of Technology, 12 March 1982.

5. P. M. Dehmer, "Systematics of Electronic Structure Within Families of van der Waals Molecules," Optical Physics - Chemical Physics Seminar, University of Maryland, 20 April 1982.

6. P. M. Dehmer, "Dissociation in Small Molecules," Discussion Leader, First International Workshop on Desorption Induced by Electronic Transitions (DIET-I), Williamsburg, VA, 12-14 May 1982.

7. P. M. Dehmer, "Systematics of Electronic Structures Within Families of van der Waals Molecules," Chemistry Department Seminar, University of Illinois at Chicago Circle, 18 May 1982.

8. J. L. Dehmer, "Molecular Photoionization Dynamics - Progress and Prospects," Physics Colloquium, University of Chicago, 27 May 1982.

9. P. M. Dehmer, "Molecular Spectroscopy - Where are the New Frontiers?", Programmatic Division Directors' Talk, Argonne National Laboratory, 7 June 1982.

10. J. L. Dehmer, "Overview of Experimental and Theoretical Studies of Resonance Processes in Molecular Photoionization by Single-Photon and Multiphoton Excitation," Gordon Research Conference on Electron Spectroscopy, Wolfeboro, New Hampshire, 19 July 1982.

11. P. M. Dehmer, "VUV Spectroscopy of Rare Gas van der Waals Dimers," NATO Advanced Study Institute on Photophysics and Photochemistry in the Vacuum Ultraviolet, Lake Geneva, Wisconsin, 19 August 1982.

12. P. M. Dehmer, "VUV Spectroscopy of van der Waals Dimers and Heavier Clusters," 2nd European Workshop on Molecular Spectroscopy and Photon-Induced Dynamics, Flevopolder, The Netherlands, 27 September 1982.

13. J. L. Dehmer, "Multiphoton Ionization as a Probe of Molecular Photoionization Dynamics," U.S./Japan Seminar on Electron-Molecule Collisions and Photoionization Processes, Pasadena, California, 26 October 1982.

INVITED TALKS, COLLOQUIA, AND SEMINARS, Continued

14. J. L. Dehmer, "Resonant Processes in Molecular Photoionization," Meeting of the American Physical Society, Los Angeles, CA, 24 March 1983.

15. P. M. Dehmer, "Photoelectron Spectroscopy Following Resonantly Enhanced Multiphoton Ionization," Workshop on Experiments, Argonne National Laboratory, 16 April 1983.

16. P. M. Dehmer, "Decay of Rydberg States via Autoionization and Predissociation," Fourteenth Meeting of the Division of Electronic and Atomic Physics, Boulder, CO, 23 May 1983.

7. Extenuating Circumstances

None.

8. Unspent Funds

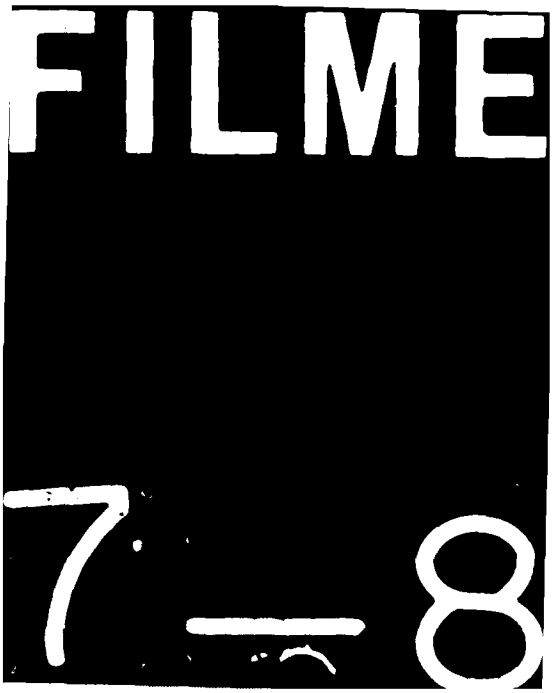
None.

9. Graduate Students Receiving Degrees

None.

10. Other Federal Contract Support

J. L. Dehmer is a co-principal investigator on Office of Naval Research Contract N00014-83-F-0005, "Triply Differential Studies of Atomic and Molecular Photoionization Using Synchrotron Radiation," 10/1/82 - 9/30/83.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